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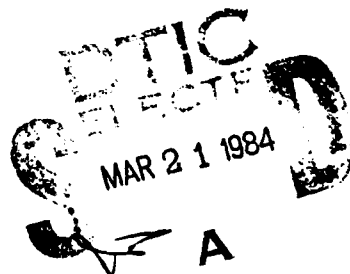AEROSOL DIRECT FLUORINATION: ALKYL HALIDES II, CHLORINE SHIFTS

AND THE STABILITY OF RADICALS

by

James L. Adcock and
William D. Evans

Department of Chemistry
University of Tennessee
Knoxville, Tennessee 37996-1600

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Beta Chloroalkyl Radicals

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

Unlike alkyl bromides and iodides, alkyl chlorides are shown to be stable to direct fluorination, even under ultraviolet irradiation, at temperatures of 30°C and below. Although less reactive than the bromides and iodides, F-alkyl chlorides may be derivatized presenting another example of direct fluorination-survivable functionality. High (63%) to moderate (32%) isolated yields of the analogous perfluoroalkyl chlorides can be synthesized by aerosol direct fluorination of 1-chloropropane, 1-chlorobutane, 1-chloro-2-methylpropane, 1-chloro-3-methylbutane, 1-chloro-2-methylbutane and chloro-cyclopentane

Abstract (continued)

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Tertiary alkyl chlorides generally undergo intramolecular 1,2-chloride shifts in the earliest stages of reaction in a manner characteristic of beta chloro radicals forming principally primary F-alkyl chlorides. Thus 2-chloro-2-methylpropane produces 1-chloro-F-2-methylpropane (47%), and 2-chloro-2-methylbutane produces a 16:6.3:1 ratio of 1-chloro-F-2-methylbutane, 1-chloro-F-3-methylbutane and 2-chloro-F-3-methylbutane respectively in 32% combined yield.

Secondary alkyl chlorides undergo a similar but incomplete rearrangement producing mixtures of primary and secondary F-alkyl chlorides. Thus 2-chloropropane produces a 2:1 mixture of 2-chloro-F-propane and 1-chloro-F-propane in 50% combined yield; 2-chlorobutane produces a 1:1.5 mixture of 2-chloro-F-butane and 1-chloro-F-butane in 34% combined yield, and 3-chloro-pentane produces a 2:3:1 mixture of 3-chloro-F-pentane, 2-chloro-F-pentane and 1-chloro-F-pentane respectively in a combined yield of 30%. Because secondary alkyl chlorides partially rearrange but primary alkyl chlorides do not rearrange at all on fluorination, doubt is cast on the postulate that the intermediate radicals are equilibrating.

Aerosol Direct Fluorination: Alkyl Halides II, Chlorine Shifts

and the Stability of Radicals

by

James L. Adcock* and
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Department of Chemistry
The University of Tennessee
Knoxville, Tennessee 37996-1600

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The fluorination of compounds with survivable functionality permits the
preparation of fluorinated compounds with preselected sites for further
reaction. The survivability of acyl fluorides,[1,2] ethers,[3,4] ketals,[4]
and to a lesser extent, esters[1] and amines[5,6] to elemental fluorine
attack are well documented in the literature. More recently reliable
ketone direct fluorinations have been documented[7] although isolated cases
of direct fluorination syntheses of ketones, albeit in poor yields, have
been noted previously.[8] The stability of perfluoroketones to photochem-
ically finished aerosol direct fluorination is remarkable given their known
photolability.[9]

Perhaps the most useful monovalent substituent groups on perfluorocar-
bons are the iodides.[10] Perfluoroalkyl bromides are less reactive and are
rarely used if the iodides are available. However neither of these substi-
tuents will survive attack by elemental fluorine. Until the recent aerosol
direct fluorination of neopentyl chloride the useful survivability of a
chloro group was in doubt.[11] Many previous attempts to direct fluorinate
alkyl chlorides resulted in extensive fragmentation, chlorine loss and
significant free radical chlorination competing with fluorination.[12-19]
For example, the reaction of elemental fluorine with 1,2-dichloropropane at
$100°-200°C$ gave large amounts of CF_4, C_2F_6 and C_3F_8 as well as small amounts
of 1,2-dichloro-F-propane, 1,3-dichloro-F-propane and materials containing
three or more chlorines.[20] The ease with which the C-Cl bond was cleaved

and the degree of free radical chlorination giving rise to polychlorinated products were in retrospect obviously a result of the high temperatures involved. In contrast to the above works this work demonstrates the exceptional stability of a number of chloroalkanes toward fission of the C-Cl bond by photochemically finished aerosol direct fluorination. The predictable occurence of 1,2-chloride shifts giving rearranged products in some instances has been studied systematically as well.

RESULTS & DISCUSSION

A previous contribution in the area of aerosol direct fluorination of alkyl halides, showed that alkyl chlorides underwent exclusively free radical attack by elemental fluorine.[11] This is in contrast to the carbocation generation which occured, at least initially, when alkyl bromides were subjected to aerosol direct fluorination.[11] The extremely low degree of C-Cl bond fission occurring in the aerosol fluorination of neopentyl chloride prompted us to look more extensively into the aerosol direct fluorination of other alkyl chlorides as a means by which preselected, survivable sites for subsequent reaction could be incorporated into organic molecules prior to their fluorination.

The aerosol direct fluorination process has been described in detail elsewhere.[4,7] The process is a steady state flow process in which a hydrocarbon vapor is condensed onto a sodium fluoride preaerosol and then subjected to attack by a 50% to 100% excess over the stoichiometric amount of elemental fluorine at low (2-5%) concentration in helium at low (-70° to 0°C) temperatures in the dark. The partially (50% to 70%) fluorinated hydrocarbons are then subjected to ultraviolet irradiation at ambient fluorine concentrations to remove residual hydrogen atoms. Partial fluorination runs are conducted under precise stoichiometric control usually without photochemical finishing.

Primary alkyl chlorides such as n-propyl chloride, n-butyl chloride and
isobutyl chloride show exceptional stability to both elemental and photo-
chemically generated atomic fluorine (Table 1). In contrast, the aerosol
direct fluorination of tertiary alkyl chlorides results in a 1,2-chloride
shift giving primary perfluoroalkyl chlorides (Table I). For example in the
aerosol fluorination of tert-butyl chloride, complete conversion to F-iso-
butyl chloride is observed. No fluorinated tertiary chlorine products were
observed. A second reaction with only 6 mmol/h of fluorine with 3 mmol/h.
tert-butyl chloride and without photofinishing gave unreacted tert-butyl
chloride (30%), 1-chloro-2-fluoro-2-methylpropane (30%), 1-chloro-2,3-di-
fluoro-2-methylpropane (20%), 1-chloro-1,2-difluoro-2-methylpropane (2%)
plus more highly fluorinated material (15%). The only tertiary chloride
that was observed, occured on unreacted starting material. No free chlorine
was observed, nor were any products found to contain more than one
chlorine. This reaction shows that the chloride shift occurs on radical
formation early in the fluorination. Chlorine fission due to photolysis or
fluorine displacement apparently does not occur with observable
significance.

In the aerosol fluorination of tert-amyl chloride (2-chloro-2-methyl
butane, Table I) three rearranged perfluoroalkyl chlorides were collected.
The relative, near statistical, proportions of 1-chloro-F-2-methylbutane
(43.1%) and 1-chloro-F-3-methylbutane (17.0%), while only a trace of
2-chloro-F-3-methylbutane (2.7%) was collected, shows that multiple
1,2-chloride shifts occur readily during perfluorination. Perfluoro-tert-
amyl chloride was not produced.

Secondary alkyl chlorides show intermediate stability when fluorinated
giving both primary and secondary perfluoroalkyl chlorides (Table I).

Table 1

AEROSOL DIRECT PERFLUORINATIONS OF CHLOROALKANES

Starting Compound	Product 1	Effluent concn. %	Yield %[a]	Product 2	Effluent concn. %	Yield %	Product 3	Effluent concn. %	Yield %
1-Chloropropane	1-Chloro-F-propane	85	63						
1-Chlorobutane	1-Chloro-F-butane	60.2	42.4	F-butane		b	Hydryl-1-Chloro-F-butanes		b
1-Chloro-2-methylpropane	1-Chloro-F-2-methylpropane	76.4	41	F-2-methylpropane	15.6				
1-Chloro-3-methylbutane	1-Chloro-F-3-methylbutane	67	32	F-2-methylbutane	19	—		—	
1-Chloro-2-methylbutane	1-Chloro-F-2-methylbutane	66	39	F-2-methylbutane	19	—		—	
2-Chloro-2-methylpropane	1-Chloro-F-2-methylpropane	80.4	47						
2-Chloro-2-methylbutane	1-Chloro-F-2-methylbutane	43.1	c	1-Chloro-F-3-methylbutane	17.0	c	2-Chloro-F-3-methylbutane	2.7	c
2-Chloropropane	2-Chloro-F-propane	52	d	1-Chloro-F-propane	28	d			
2-Chlorobutane	2-Chloro-F-butane	30	e	1-Chloro-F-butane	43	e			
3-Chloropentane	3-Chloro-F-pentane	30	f	2-Chloro-F-pentane	45	f	1-Chloro-F-pentane	15	f
Chlorocyclopentane	Chloro-F-cyclopentane	49.5	40.2	F-cyclopentane	12.5	f	F-pentane[g]	12.5	f

(a) Yield's are based on total starting compound injected which are not corrected for recovered unreacted starting material collected at the close of the reaction; (b) combined yield 6.9%; (c) combined yield 31.8%; (d) combined yield 50%; (e) combined yield 34%; (f) combined yield 30%; (g) three isomeric chloro-F-pentanes make up 15.5% of effluent.

Evidence for multiple 1,2-chloride shifts are seen again in the perfluori-
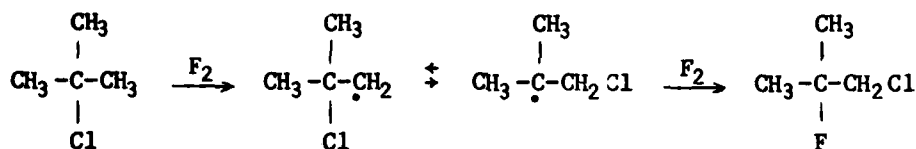nation of 3-chloropentane.

These results are for the most part supported by literature accounts of
rearrangements associated with free radical reactions. For example, Skell,
Allen and Gilmour observed that chlorination of 2-bromopropane and 2-bromo-
2-methylpropane produced 1-bromo-2-chloropropane and 1-bromo-2-chloro-2-
methylpropane respectively.[21] These findings indicated complete
rearrangement. An initial hydrogen abstraction from one of the methyl
groups leading to a primary radical was immediately followed by a 1,2-bro-
mide migration to form a more stable tertiary radical which then added
chlorine to form the rearranged products. Juneja and Hodnett observed the
same 1,2-bromide shift in the chlorination of 2-bromo-2-methylpropane as did
Skell, et. al.[22] They also observed that no rearrangement occured in the
chlorination of 1-bromo-2-methylpropane. The latter rearrangement would not
be expected to occur as it would involve forming a primary radical from a
tertiary radical. Formation of a tertiary radical is also statistically
unfavorable.

Wiley, et. al., noted the isomerization of 1-chloropropane to
2-chloropropane during radiolysis but not the reverse reaction.[23] This
seeming contradiction was re-investigated by Benson and Willard who observed
that this reaction was catalyzed by hydrogen chloride and that the hydrogen
atom exchanges, not the chlorine atom.[24] Mayo postulated that an equili-
brium between secondary and primary radicals could explain this rearrange-
ment.[25] If the reactions of these radicals require little or no activation
energy, the products will conform to the more stable radical. However if
the reactions of these radicals require a large activation energy and are
therefore relatively difficult, then the products will conform to those

derived from the minor proportions of the less stable, but more reactive radical. In this way the seeming contradiction is resolved; i.e. only the more reactive radicals formed by radiolysis, C-H bond fission, will react with HCl to produce the observed product because of the relatively high activation energy required.

The above postulate would also explain why products derived from the interactions of intermediate free radicals with fluorine molecules, a low activation energy process, should predominately correspond to those derived from the more stable radicals. Other free radical rearrangements involving 1,2-chloride shifts have been reviewed by Freidina.[26]

When a 1:2 molar ratio of tert-butyl chloride to fluorine aerosol fluorination was carried out 1-chloro-2-fluoro-2-methylpropane was the major product observed. This suggests a mechanism (Scheme I) similar to that

$$CH_3-\underset{\underset{Cl}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_3 \xrightarrow{F_2} CH_3-\underset{\underset{Cl}{|}}{\overset{\overset{CH_3}{|}}{C}}-\overset{\bullet}{C}H_2 \Longleftrightarrow CH_3-\underset{\bullet}{\overset{\overset{CH_3}{|}}{C}}-CH_2Cl \xrightarrow{F_2} CH_3-\underset{\underset{F}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_2Cl$$
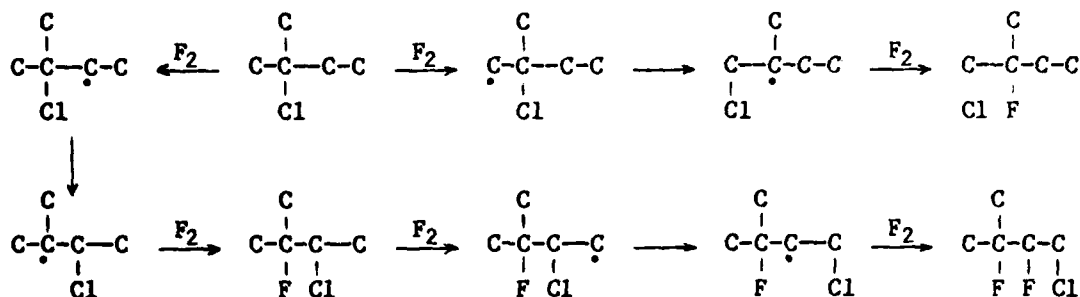
Scheme I

observed by Skell, et. al. in which initial H abstraction from a methyl group results in a rapid 1,2-chloride shift to produce a more stable tertiary radical.[21] This could occur by the formation of a bridged radical intermediate (below) which would open preferentially to the more

$$(CH_3)_2\overset{\bullet}{C}\underset{\overset{\cdot}{Cl}}{-\!\!-\!\!-}CH_2$$
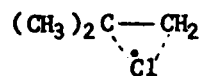
stable tertiary radical.[27] If Mayo's postulate is general, the concentration of the tertiary radical would far exceed that of the primary radical giving the observed primary F-alkyl chloride. This postulate also explains

the lack of rearrangements encountered during the fluorination of primary alkyl chlorides having alpha tertiary hydrogens.

In the analogous fluorination of tert-amyl chloride, the tertiary-chlorine can rearrange from a 1° to 3° radical by a 1,2-chloride shift giving the primary F-alkyl chloride. However, the tertiary chloride can also rearrange by a 1,2-chloride shift giving a secondary chloride if the initial radical is formed by H abstraction at the methylene group. The secondary chloride can subsequently rearrange by a second 1,2-chloride shift giving the other possible primary alkyl chloride, 1-chloro-F-3-methylbutane, if a subsequent hydrogen abstraction by fluorine occ⌐ on the 3-methyl group adjacent to the methylene group (Scheme II). ⌐ s final shift would occur, however, only if the 3-methyl group has not b⌐ n ⌐eviously fluorinated.

Scheme II

The partial rearrangement of secondary alkyl chlorides during fluorination can also be rationalized by Mayo's postulate.[25] However in the case of equilibrium between primary and secondary alkyl radicals, the concentration of secondary radical would not be so predominant nor would their reactivity differ as much. The more similar concentrations would therefore result in a mixture of products representing both rearranged and unrearranged products. The problem with Mayo's rationalization is that it should

work in reverse, i.e. when primary alkyl chlorides are fluorinated some secondary alkyl chloride should be isolated. Since this does not occur, there must be kinetic and/or other effects operating. This observation certainly casts some doubt on Mayo's postulation and a more careful look at the problem is indicated.

EXPERIMENTAL

The basic aerosol fluorinator design and a basic description of the process are presented elsewhere.[4,7] Detailed parameters for reactor variables are given in Table 2. Workup of products following removal of the hydrogen fluoride formed during the fluorination consisted of vacuum line fractionation; infrared assay of fractions; gas chromatographic separation of components using either a 7 meter x 3/8" 13% Fluorosilicone QF-1 (Analabs) stationary phase on 60-80 mesh, acid washed, Chromosorb p conditioned at 225°C (12-h) or a 4 meter x 3/8" 10% SE-52 phenyl-methyl silicone rubber on acid washed 60-80 mesh Chromosorb p, conditioned at 250°C (12-h). Following gas chromatographic separation (Bendix Model 2300, subambient multi-controller) all products of "significance" were collected, transferred to the vacuum line, assayed and characterized by vapor phase infrared spectrophotometry, PE1330; electron impact (70eV) and chemical ionization (CH_4 plasma) mass spectrometry (Hewlett-Packard GC/MS, 5710A GC, 5980 A MS, 5934A Computer); and ^1H and ^{19}F nuclear magnetic resonance (JEOL FX90Q, omniprobe) in $CDCl_3$ with 1% $CFCl_3$ internal standard.

Aerosol Fluorination of n-Propyl Chloride 1-Chloropropane (Matheson) has a vapor pressure at -45°C such that a helium flow of 75 mL/m produces a throughput of 0.24g/h (3.0 mmol/h). A 2 hour run produced 0.909g of crude material after fractionation. Separation isothermally at -20°C on the SE-52 column gives 1-chloro-F-propane (85%) at retention time of 6 m (rt = 6m).

TABLE 2

TYPICAL AEROSOL FLUORINATION REACTION PARAMETERS[a]

Starting Compound	Fluorine Flow mL/m Reactor Mod. 1	Mod. 2	Helium Diluent mL/m Reactor Mod. 1	Mod. 2	Reaction Temp. °C Reactor Mod. 1	Mod. 2	Main Helium Carrier mL/m	Hydrocarbon Throughput millimoles/hr (H.C.carrier)	Overall[b] Stoichiometry hc:F_2	Percent F_2 Conc. Final Stage	Reaction Time[e] Sec.	Product[d] Effluent concn. % Collected	Product[d] Yield % Theoretical
n-Propyl Chloride	15	15	80	80	-40°	-0°	1000	3.0 (75)	1:25	2.4	65	85%	63%
iso-Propyl Chloride	20	20	80	80	-40°	-0°	800	4.0 (75)	1:25	3.9	75	80%	50%e
n-Butyl Chloride	20	20	80	80	-45°	10°	1000	3.1 (48)	1:42	4.4	60	60.2%	42.2%
Iso-Butyl Chloride	20	-	80	-	-45°	10°	1000	1.4 (20)	1:54	3.2	66	76.4%	41.2%
sec-Butyl Chloride	19	19	75	75	-45°	10°	1000	2.8 (33)	1:46	4.5%	61	72.8%	32.8%f
tert-Butyl Chloride	20	20	70	70	-40°	10°	1000	3.0 (13)	1:45	4.7%	63	80.4%	46.5%g
tert-Butyl Chloride	2.5	-	70	-	-45°	10°	800	3.0 (13)	1:2	0.3	91	-	— h
1-Chloro-3-methylbutane	20	20	80	80	-40°	0°	1000	3.0 (12)	1:40	45	62	67%	32%
1-Chloro-2-methylbutane	20	20	80	80	-40°	0°	1000	3.0 (12)	1:40	4.5	62	66%	39%
3-Chloropentane	20	20	80	80	-45°	10°	1000	1.2 (20)	1:122	4.5	62	90%	31%i
tert-Amyl Chloride	20	30	80	120	-40°	10°	800	2.5 (53)	1:44	4.5%	74	62.8%	31.8%
Cyclopentyl Chloride	20	20	80	80	-40°	10°	1000	2.0 (135)	1:73	4	57	49.5%	40.2%

(a) See references 4 and 7 for significance, meaning of parameters (Mod = Module). (b) 1.0 mL/m F_2 delivers 2.44 mmol/h F_2. (c) Reactor volume 1.355 L. (d) All isomers
(e) F-n-Propyl Chloride plus 33% F-iso-Propyl Chloride. (f) 13% F-n-Butyl chloride plus 19.8% F-sec-Butyl Chloride. (g) F-iso-Butyl Chloride. (h) Mixture, non
photochemically finished, UV lamp off, non perfluorinated products. (i) 10.3% 3-Chloro-F-pentane, 15.5% 2-Chloro-F-pentane, and 5.2% 1-Chloro-F-pentane.

This corresponds to a 63% yield based on theoretical throughput. The IR spectrum matches that published.[28]

Aerosol Fluorination of iso-Propyl Chloride: 2-Chloropropane (Eastman) has a vapor pressure at -45°C such that a helium flow of 75 mL/m produces a throughput of 0.31g/h (4.0 mmol/h). A 2.5 h run produced 1.2393g of crude product after fractionation. Separation isothermally at -20°C on the SE-52 column gives an unresolved peak (80%) (rt = 6 m). A second separation on the QF-1 column a broad peak (80%) (rt = 18 m). This mixture corresponds to 48.5% of the calculated yield. The IR spectrum shows a 1:2 mixture of 1-chloro-F-propane and 2-chloro-F-propane matching those published.[28,29]

Aerosol Fluorination of n-Butyl Chloride: 1-Chlorobutane (Fisher Scientific) was used as received. Its vapor pressure at -10°C is such that a flow of 58 mL/m helium through -50 mL of the material contained in a sparge tube evaporator produces a throughput of 0.29g/h (3.15 mmol/h). For a 2 h photochemically finished run, 1.1676g of crude product was collected after vacuum line fractionation. Purification of the products on the GC SE-52 column (0°C/5 m; 10°C/m to 30°C; 25°C/m to 180°C/10 m) produced 6.9% F-n-butane (rt = 3 m) and 60.2% 1-chloro-F-butane (Cmpd 1) (rt = 6 m). The yield of Cmpd 1 based on the calculated throughput was 43.8%. IR of Cmpd 1 (cm^{-1}): 1351(m), 1285(sh), 1240(vs), 1213(vs), 1160(w), 1148(s), 1110(s), 1020(sh), 997(m), 866(m), 848(sh), 802(s), 745(sh), 732(s), 694(m). ^{19}F NMR (1% $CFCl_3/CDCl_3$): (multiplicity, relative area) $CF_3{}^ACF_2{}^BCF_2{}^CCF_2{}^DCl$, ϕ_A = -81.7 ppm (t·t, 3); B -126.1 (t·m,2); C -121.6 (q·m,2); D -68.9 (t·q,2); $J_{AB} = J_{AD}$ = 1.1 Hz, J_{AC} = 9.89 Hz, J_{BD} = 12.64 Hz, J_{CD} = 1.46 Hz. Major mass cations were [m/e(int)Formula]: [EI] 237(25.4)$C_4F_8{}^{37}Cl$, 235(77.6)$C_4F_8{}^{35}Cl$, 219(100)C_4F_9, 149(5.2)$C_3F_4{}^{37}Cl$, 147(17.5)$C_3F_4{}^{35}Cl$, 131(9.6)C_3F_5, 119(12.2)C_2F_5, 87(4.4)$CF_2{}^{37}Cl$, 85(15.2)$CF_2{}^{35}Cl$, 69(2.7)CF_3.

Aerosol Fluorination of iso-Butyl Chloride 1-Chloro-2-methylpropane
(Eastman) has a vapor pressure at -10°C such that a helium flow of 25 mL/m
produces a throughput of 0.13g/h (1.4 mmol/h). A 2 h run produced 0.3881g
of crude material after fractionation. Separation on the SE-52 column
(0°C/5 m; 15°C/m; 25°C/m to 200°C/10 m) gave 15.6% F-iso-butane (rt = 3 m),
and 76.4% F-isobutyl chloride (Cmpd 2) (rt = 6 m). This corresponds to a
4 1.6% yield for Cmpd 2. IR of Cmpd 2 (cm^{-1}): 1300(sh), 1280(vs), 1195(s),
1162(s), 1070(w), 1042(m), 988(s), 916(m), 863(s), 751(m), 722(ms). ^{19}F NMR
(1% CFCl$_3$/CDCl$_3$): $(CF_3{}^A)_2 CF^B CF_2{}^C Cl$ ϕ_A = -73.0 ppm (t·d,6); B -178.5
(hept·d,1); C -62.0 (t·hept,2); J_{AB} = 10.74 Hz, J_{AC} = J_{BC} = 5.88 Hz.
Major mass cations were [m/e(int) Formula]: 237(24.2)$C_4 F_8{}^{37}Cl$,
235(77.1)$C_4 F_8{}^{35}Cl$, 219(100)$C_4 F_9$, 197(23.8)$C_4 F_6{}^{35}Cl$, 131(5.1)$C_3 F_5$,
87(3.7)$CF_3{}^{37}Cl$, 85(11.8)$CF_2{}^{35}Cl$.

Aerosol Fluorination of sec-Butyl Chloride 2-Chlorobutane (Eastman) has
a vapor pressure at -10°C such that a helium flow of 33 mL/m produces a
throughput of 0.26g/h (2.8 mmol/h). A 3 h run produces 0.9708g of crude
product after fractionation. Separation on the SE-52 column with the same
program as for F-n-butyl chloride gives two overlapping peaks (rt = 5.5 to 6
m) consisting of (30%) 2-chloro-F-butane (Cmpd 3) and (43%) 1-chloro-F-
butane (Cmpd 1). The calculated yield of Cmpd 1 was 19.5%. The yield of
Cmpd 3 was 13.69%. ^{19}F NMR of Cmpd 3 (1% CFCl$_3$/CDCl$_3$): $CF_3{}^A CF^B ClCF_2{}^C CF_3{}^D$
ϕ_A = -78.1 ppm (q·t,3); B -139.2 (t·q,1); C -121.1 (q·q,2); D -79.6 ppm
(q·d,3); J_{AC} = 10.99 Hz, J_{BD} = 9.77 Hz, J_{AD} = 3.66 Hz. Major mass cations
were [m/e(int)Formula]: 237(23.1)$C_4 F_8{}^{37}Cl$), 235(75.3)$C_4 F_8{}^{35}Cl$,
219(100)$C_4 F_9$, 185(1.6)$C_3 F_6{}^{35}Cl$; 169(8.4)$C_3 F_2$, 131(6.1)$C_3 F_5$, 119(7.9)$C_2 F_5$,
69(41.8)CF_3.

Aerosol Fluorination of tert-Butyl Chloride: 2-Chloro-2-methylpropane
(Eastman) has a vapor pressure at -10°C such that a helium flow of 13 mL/m

produces a throughput of 0.28g/h (3.0 mmol/h). A 2 h run produced 0.8884g of crude material after fractionation. Separation of the fraction on the SE-52 column with the isobutyl chloride program gave 79.49% F-iso-butyl chloride (Cmpd 2) (rt = 6 m) a 46.8% yield of the calculated throughput. No products were found which matched published IR & ^{19}F NMR spectra of F-tert-butyl chloride.[30] A second 2 h run with the same throughput and only 3.0 mmol/h fluorine flow and no photochemical finishing gave 0.513g of partially fluorinated materials. Identifiable compounds produced were: 30% unreacted starting material, 30% 1-chloro-2-fluoro-2-methylpropane,[31] 20% 3-chloro-1,2-difluoro-2-methylpropane (Cmpd 4), and 2% 1-chloro-1,2-difluoro-2-methylpropane (Cmpd 5). The yield of Cmpd 4 is 13%. ^{19}F NMR of Cmpd 4 (1% CFCl$_3$/CDCl$_3$):(F^{A}CH$_2$^{C})CF^B(CH$_2$^{D}Cl)(CH$_3$^{E}) ϕ_A = -244 ppm (m·t,1), B -185 (m,1); J_{AB} = 9 Hz; ^{1}H NMR (0.2% CHCl$_3$/CDCl$_3$) δ_C = 4.45 ppm (d·d,2), D 3.65 (d·m, 2), E 1.45 (d·d,3); J_{AC} = 47 Hz, J_{BC} = J_{BD} = J_{BE} = 19 Hz, J_{AD} = J_{AE} = 2 Hz. The yield of Cmpd 5 is 1.3%: ^{19}F NMR of Cmpd 5 (1% CFCl$_3$/CDCl$_3$): CF^{A}H^{C}ClCF^B(CH$_3$^{D})$_2$ ϕ_A = -144 ppm (m·d,1), B -187 (m,1); J_{AB} = 9 Hz; ^{1}H NMR (0.2% CHCl$_3$/CDCl$_3$), δ_C = 5.95 ppm (d·d,1), D 1.45 (m·d,6); J_{AC} = 56 Hz, J_{BD} = 19 Hz, J_{BC} = 9 Hz, J_{AD} = 2 Hz.

Aerosol Fluorination of 1-Chloro-3-methylbutane: 1-Chloro-3-methyl-butane has a vapor pressure at 220°C such that a helium flow of 12 mL/m produces a throughput of 0.42g/h (3.0 mmol/h). A 3 h run produced 1.323g of crude product. Separation on the SE-52 column (15°C/5 m; 10°C/m to 75°C/0 m; ⁻0°C/m to 160°C/10 m) gave 19% F-isopentane and 67% 1-chloro-F-3-methyl- 'Cmpd 6) (rt = 7 m). The yield of Cmpd 6 is 32%. IR of Cmpd 6 300(sh), 1260(vs), 1250(vs), 1225(vs), 1180(s), 1145(m), 1100(s), 9/⌐(v)., 740(m), 710(m). ^{19}F NMR (1% CFCl$_3$/CDCl$_3$): (CF$_3$^{A})$_2$CF^{B}CF$_2$^{C}CF$_2$^{D}Cl ϕ_A = -72.8 ppm (m,6), B -185.7 (m,1), C -113.2 (m,2), D -68.3 (m,2). Major mass cations were [m/e(int)Formula]: 287(10.3)C$_5$F$_{10}$^{37}Cl, 285(32.1)C$_5$F$_{10}$^{35}Cl,

J_{AB} = 12.2 Hz, J_{CE} = 4.5 Hz; Cmpd $\underline{10}$ $CF_2{}^ACICF_2{}^BCF_2{}^CCF_2{}^DCF_3{}^E$ ϕ_A = -68.6 ppm (t,2), B -120.8 (m,2); C -122.6 (m,2); D -126.7 (m,2); E -81.2 (t,3); J_{AC} = 12.2 Hz, J_{CE} = 12.2 Hz.

Aerosol Fluorination of tert-Amyl Chloride: 2-Chloro-2-methylbutane (Eastman) has a vapor pressure at 0°C such that a helium flow of 53 mL/m produces a throughput of 0.27g/h (2.5 mmol/h). A 2.5 h run produced 0.9626g of crude material after fractionation. Separation on the SE-52 column (15°C/5 m; 10°C/m to 75°C; 50°C/m to 180°C/10 m) gives 6.2% F-isobutane, (rt = 3 m), 22.1% F-isopentane (rt = 3.5 m), and 62.8% of an unresolved mixture (16:6.5:1) (rt = 7 m), of 1-chloro-F-2-methylbutane (Cmpd $\underline{7}$), 1-chloro-F-3-methylbutane, (Cmpd $\underline{6}$), and 2-chloro-F-3-methylbutane (Cmpd $\underline{11}$). No 2-chloro-F-2-methylbutane was observed. The ^{19}F NMR spectrum of Cmpd $\underline{11}$ is (1% $CFCl_3$/$CDCl_3$):$(CF_3{}^A)_2CF^BCF^CCICF_3{}^D$ ϕ_A = -70.7 ppm (m,6), B -176.0 (m,1), C -135.3 (m,1), D -77.8 (m,3).

Aerosol Fluorination of Chlorocyclopentane: Chlorocyclopentane (Aldrich) has a vapor pressure at -10°C such that a helium flow of 135 mL/m produces a throughput of 0.21g/h (2.0 mmol/h). A 3 h run produces 1.30g of crude product after fractionation. Separation on the QF-1 column (10°C/13 m; 10°C/m to 60°C/5 m; 50°C/m to 180°C/5 m) gives 2.6% F-butane (rt = 5 m), 12.5% F-cyclopentane (rt = 12 m), 5% $C_4F_{11}Cl$ (Cmpds $\underline{1}$&$\underline{3}$) (rt = 15 m), 12.5% F-pentane (rt = 18 m), 49.5% 1-chloro-F-cyclopentane (Cmpd $\underline{12}$) (rt = 22 m), and 15.5% unresolved $C_5F_{11}Cl$ isomers (Cmpds. $\underline{8}$,$\underline{9}$,$\underline{10}$) (rt = 25-26 m). The yield of Cmpd $\underline{12}$ is 40.2%. IR of Cmpd $\underline{12}$ (cm^{-1}) 1310(s), 1275(m), 1240(s), 1220(vs), 1120(m), 1065(vw), 1020(m), 970(s), 920(w), 870(s), 740(w); ^{19}F NMR (1% $CFCl_3$/$CDCl_3$): $\phi CFCl$ = -139.8 ppm (m,1) ϕCF_2 = -118.0 and -136.5 ppm (A B pattern, 2,5- and 2',5'-, $J_{22'}$ = $J_{55'}$ = 262.5 H_z, 4) ϕCF_2 = -126.5 and -129.0 ppm (A B pattern, 3,4- and 3',4'-, $J_{33'}$ = $J_{44'}$ = 253.3

H_z, 4). Major mass cations were [m/e(int)Formula] $199(31)C_4F_6{}^{37}Cl$, $197(100)C_4F_6{}^{35}Cl$, $149(40)C_3F_4{}^{35}Cl$, $131(56)C_3F_5$, $100(22)C_2F_4$.

Acknowledgement

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